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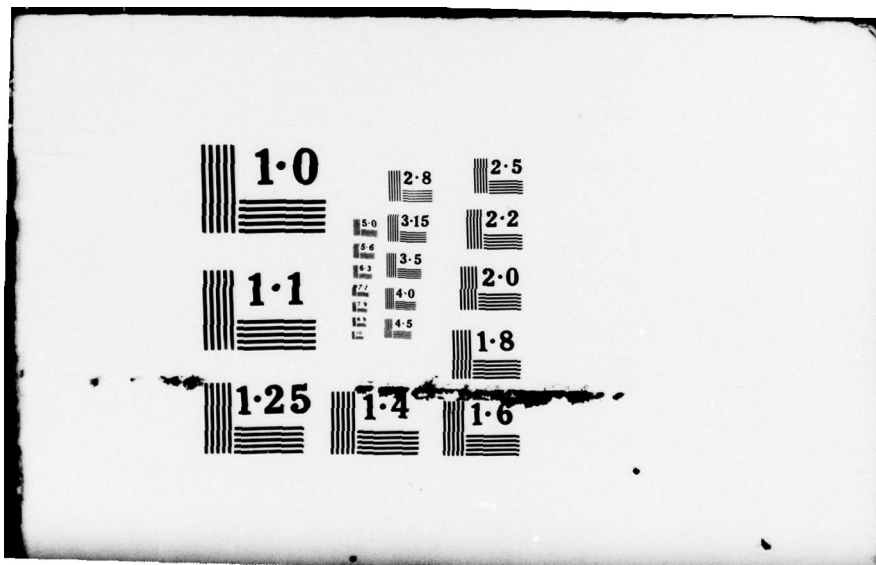
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E USE OF RADIOACTIVE J^{131} FOR DETERMINING THE CONCENTRATION
OF BARIUM IN AN OXIDE CATHODE

By

V. P. Pomazkov

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В в	*В в*	V, v	Т т	*Т т*	T, t
Г г	*Г г*	G, g	У у	*У у*	U, u
Д д	*Д д*	D, d	Ф ф	*Ф ф*	F, f
Е е	*Е е*	Ye, ye; E, e*	Х х	*Х х*	Kh, kh
Ж ж	*Ж ж*	Zh, zh	Ц ц	*Ц ц*	Ts, ts
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К к	*К к*	K, k	ъ ъ	*ъ ъ*	"
Л л	*Л л*	L, l	Ы ы	*Ы ы*	Y, y
М м	*М м*	M, m	ь ь	*ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

*ye initially, after vowels, and after ъ, ь; e elsewhere.
When written as ё in Russian, transliterate as yё or ё.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

| Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	$\sinh^{-1}$
cos	cos	ch	cosh	arc ch	$\cosh^{-1}$
tg	tan	th	tanh	arc th	$\tanh^{-1}$
ctg	cot	cth	coth	arc cth	$\coth^{-1}$
sec	sec	sch	sech	arc sch	sech^{-1}
cosec	csc	csch	csch	arc csch	csch^{-1}

Russian	English
rot	curl
lg	log

THE USE OF RADIOACTIVE J^{131} FOR
DETERMINING THE CONCENTRATION OF
BARIUM IN AN OXIDE CATHODE

V. P. Pomazkov

At the present time an oxide cathode is the most popular type of a cathode. Most of the theoretical and experimental studies devoted to the oxide cathode result in a firm conviction that the useful properties of oxide cathodes (low work function, high stability, high efficiency, etc.) are ensured by the excess of a free alkaline-earth metal.

Beginning in the thirties a considerable attention was devoted to determining the concentration of the free alkaline-earth metal. A whole series of methods was employed whose comparative characteristic is given in [1]. Most of these methods were based on the determination of the amount of gas liberated from an oxide coating as a result of the treatment with a certain reagent. Most of the determinations were made with the aid of the Berdennikova's method [2]. In the research stage of its operation the oxide cathode was treated with water vapors. Water reacts with the basic components of the oxide coating in the following manner:

$$Ba + 2H_2O = Ba(OH)_2 + H_2;$$
$$Ba + H_2O = BaO + H_2;$$
$$BaO + H_2O = Ba(OH)_2.$$
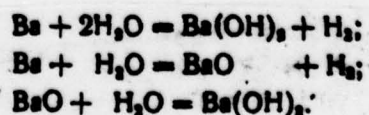
As we can see from these reactions the liberated hydrogen, by its

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nature binds only with barium. However, the application of this method to real objects becomes very complicated since very rigid requirements with respect to gas liberation are imposed on all the components of the device used to study the free barium. Furthermore, this method, just like all the rest used hitherto, allows one to measure only an integral amount of free barium on the cathode but does not permit one to study its distribution through the oxide layer. Knowing the distribution of this free barium in the oxide coating and, especially, the change in this distribution in the various stages of operation of the cathode is very important for a better understanding of its operating mechanism.

The ability of halogens to combine with the free alkaline-earth metal under certain conditions and the ability not to interact with its oxides can be used to determine the free barium. By treating the oxide layer with the vapors of a radioactive halogen and then by measuring its activity, it is possible to determine the amount of free barium. Off all the halogens the most suitable for such measurements turned out to be J^{131}. J^{131} has high specific activity as a result of which, it is possible to obtain high sensitivity which exceeds the sensitivity necessary for the determination of the possible amount of free barium in the device by several orders. In our experiments we used the sensitivity from 10^{-8} to $5 \cdot 10^{-12}$ g/imp. with respect to barium depending on the problems posed. The iodine is very convenient for vacuum purification and packaging into the necessary doses. In the operation soft beta-radiation does not require a cumbersome protection and filters out well. For the convenience of operation the usual iodine J^{127} was prepared in the form of a solution in benzene. The supplied solution of radioactive J^{131} in water was mixed with the solution of J^{127} in benzene. From the solution of marked iodine obtained in this manner the benzene was removed by means of a capillary. The crystalline iodine was subjected to vacuum sublimation 6–7 times at the pressure of $1 \cdot 10^{-6}$ mm Hg. During the sublimation the iodine was passed 2–3 times through the plugs of phosphoric anhydride for complete desiccation. At the end of the purification process the iodine was placed into small ampules (~0.5 cm^3) which can be soldered to

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the experimental device and can be easily broken during the study phase of the cathode's operation.

The cathode processing regime in iodine vapors must satisfy two basic requirements:

1. The entire amount of free barium must react with iodine.

2. The iodine must not combine with the other components of the oxide cathode.

The study of the cathode's processing conditions in iodine vapors was accomplished by comparing the activity of two completely identical cathodes one of which did not contain any free barium. The device for such measurements consisted of two completely identical tubes, a vessel with desiccated oxygen, ampules with iodine, and a manometer (Fig. 1). Each tube represented a diode with an end cathode. The anode was constructed in the form of a nickel diaphragm whose opening was exactly opposite the cathode's coating and could be closed with a nickel gate which is easily moved by a magnet. The upper part of the tube's bulb was made in the form of a thin glass hemisphere. The thickness of the nickel diaphragm and the gate was selected such that the beta-radiation of the J^{131} would be absorbed completely. On the other hand, the thickness of the glass was selected such that the absorption coefficient of the J^{131} radiation would not exceed 4. Such a construction made it possible to measure the iodine's activity on the cathode with considerable accuracy without opening up the tube. The advantage of such a determination of the iodine's activity in the coating is the fact that all changes in activity and, consequently, also the degree of "etching" of free barium are determined from one sample. The vacuum treatment of the device was carried out as follows:

1. Evacuation of the device in a furnace at 420°C to obtain a vacuum of $(2-4) \cdot 10^{-6}$ mm Hg.

2. Slow decomposition of carbonates on both cathodes at a vacuum of not worse than $5 \cdot 10^{-5}$ mm Hg.

3. Activation of cathode No. 1 at 960–980°C until good emission is obtained.

4. Unsoldering the device from the vacuum system and the admission of oxygen from the vessel.

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5. Heating of cathode No. 1 for 5 min in oxygen atmosphere at a pressure of several millimeters of mercury and the temperature of the cathode at 600°C. As was demonstrated by the experiment, leting in the oxygen without preheating the cathode does not "etch out" completely the entire free barium on the cathode.

6. After the preheating of the cathode a thin glass diaphragm Π was shattered (see Fig. 1) and the entire device was again evacuated down to $(1-2) \cdot 10^{-6}$ mm Hg.

7. Activation of cathode No. 2 at a vacuum of not worse than $2 \cdot 10^{-6}$ mm Hg.

8. Unsoldering of the entire device from the vacuum system and the admission of iodine.

9. Measurements of the activity from the cathodes began immediately after the unsoldering. The measurements were taken by the endwindow counter, BFL-T-25. During the measurements the iodine was frozen out into ampule A (see Fig. 1) by liquid air to reduce the background.

Figure 2 shows the curves of change in the activity on both cathodes as a function of time and temperature. It is clear from the figure that the initial activity on cathode No. 2 is 1.5—2.0 orders higher than the initial activity of cathode No. 1. While the cathodes were exposed to iodine vapors at room temperature, we observed a gradual increase in activity on cathode No. 2 up to the point of saturation which takes place after several tens of hours. The activity of the cathode in the state of saturation is about twice as high as the initial activity. In the same time cathode No. 1 did not exhibit any significant increase in activity. The saturation on cathode No. 2 occurs faster when the temperature on the cathode is increased. At the cathode temperature of 150°C, saturation occurs in 100—120 min. For cathode No. 2 the heating to 150°C does not result in noticeable changes. However, a further increase in temperature to above 300°C leads to a linear increase with respect to time in activity on both cathodes; in this case the slope of the curves for both cathodes is approximately the same. This indicates the fact that at a temperature of over 300°C the iodine begins, somehow, to interact with the entire coating. The

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Activated cathode treated with iodine vapors looses the thermo-
electronic activity completely. However, it can be brough back to
the active state by heating it to 920°C and by freezing out the
iodine into ampule A. Thus, the entire procedure of cathode ex-
posure to iodine vapors can be repeated 2—3 times, obtaining re-
producible results in the nature of behavior of the activity. The
absolute activity in the second and subsequent activations after
the first etching of the cathode by iodine somewhat diminishes.
The decrease in activity can be explained by the evaporation of
the BaJ_2 at 920°C, and after a complete decomposition of BaJ_2 by
the evaporation of the free barium. These results show that the
optimum conditions of cathode processing in iodine vapors is its
heating at 150—180°C for two hours. The high level of activity
on cathode No. 2, which occurs 5—7 min after the admission of iodine
at room temperature, indicates the fact that the greater portion
of barium reacts with iodine very rapidly.

The procedure described in section 1 for determining the free
alkaline-earth metal in the oxide coating was used for certain
types of cathodes.

The experimental tube was a diode with an end cathode. The
cathode temperature was measured by a C-A thermocouple. The part
of the anode was played by a rotating disc-collector divided into
sectors. Such a construction of the tubes made it possible to
measure the free alkaline-earth metal not only in the cathode's
coating but also that portion of the cathode which evaporated onto
the anode at various stages of cathode activation.

The tubes were treated as follows:

1. Decomposition of the carbonate at 800°C and pressure not
worse than $5 \cdot 10^{-4}$ mm Hg.

2. Heating of the tube in the furnace at 420°C until a vacuum
of $(1-2) \cdot 10^{-6}$ mm Hg was attained.

3. Increasing the temperature to 960—980°C with a brief tap-
ping of the current to check the emission characteristics of the
cathode.

The decomposition of carbonates was accomplished gradually to
avoid the cracking of the coating, which was observed in the case

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of thin dense coatings out of fine-grained carbonate. Heating at
960—980°C lasted for 45 min. Coatings with a varied density were
tested on purest nickel and on the nickel with the addition of
calcium (NIKA).

The data for cathodes with a core made of an electrolytic
nickel are given in Table 1.

We can see from Table 1 that the concentration of free barium
in the coatings on the core consisting of an electrolytic nickel
differes little from one another. Some differences are easily ex-
plained by random deviations in the amount of the activator which
gets into the coating. In this case the activator can be the
binder remnants, CO, and other accidental impurities of the coating
which it contains in small amounts and which are used up during the
first few minutes of activation. The rapid consumption is confirmed
also by the evaporation rate. Most of the barium evaporates during
the first minutes of activation of the cathode. It can be seen
from the table that for all types of coatings the amount of the
vaporized barium exceeds the amount of barium in the coating.

Table shows the data for cathodes made out of nickel with the
addition of calcium.

It can be seen from Table 2 that the concentration of free
barium in the coating increased insignificantly. Basically, the
amount of vaporized barium increased. It can be seen from both
tables that not over 70—75% of the formed barium vaporizes for the
coating consisting of a triple fine-grained carbonate. A consider-
ably greater amount of free barium evaporates from looser coatings.
The evaporation from the dense and loose coatings differes not only
by the ratio of the remaining and vaporized barium but also by the
different evaporation rates during the various phases of activation.

The principal portion of barium vaporizes from the loose coatings
during the first 10—15 min of operation of the cathode at 960°C.
Subsequently, the evaporation rate drops rather rapidly. A different
picture is observed in the case of dense coatings. Here, the
evaporation rate remains virtually unchanged during the entire
heating period at 960°C. The results that were obtained are ex-
plained well by the Rittner theory [3].

Rittner constructs his theory on the basis of a supposition that the free barium formed in the precore region, as a result of interaction of the barium oxide with an activator, propagates through the coating in a manner of the Knudsen flow. The calculations presented in work [3] show that with such a mechanism of barium supply to the oxide, its greater portion (up to 95–97%) should evaporate from the coating and only 3–5% remains in the oxide layer. Thus, the ratio between the vaporized barium and the free barium remaining in the coating, obtained in our experiments, is a direct confirmation of reality of the expressed suppositions. In the case of a dense coating the specific weight of the vaporized barium decreases significantly. This fact is also explained well by the mechanism proposed by Rittner. The rate at which barium leaves the precore region is determined by the number of pores and their diameter. In a dense coating the porosity is considerably lower than that in a loose coating and the pore radius is smaller since the dense coating is applied with a more fine-grained carbonate. Consequently, the rate at which barium leaves the reaction zone with the activator will be lower. With a decreased rate of departure from the reaction zone with the activator the barium vapor pressure in this region increases, while the reaction rate of the barium oxide with the activator, naturally, decreases. This means that with denser coatings the activator is consumed more slowly. This result is confirmed by the evaporation rate of barium from dense coatings, which changes slowly in the time of activation. If the main portion of barium vaporizes from the loose coatings during the first minutes of activation, then from the dense coatings the evaporation occurs almost uniformly during the entire 45 min of heating at 960°C. The higher vapor pressure of the free barium in the pores of a dense coating also leads to its increased condensation on the individual crystals forming the coating. This, indeed, explains the fact that only 70–75% of the entire barium formed evaporates from the dense coatings.

Conclusions

These results permit one to draw the following conclusions:

1. The method for determining barium by means of the radioactive J^{131} can be used both to study the concentration of the free alkaline-earth metal in the coating and its evaporation. The sensitivity of the method permits one to measure reliably $5 \cdot 10^{-12}$ g of barium.

2. Knudsen's flow of barium through the pores from the core to the surface plays a decisive role during the activation process. Only that portion of barium remains in the coating which condenses on the crystals which form the boundaries of pores.

3. From the standpoint of the free barium balance the most suitable are the cathodes with a dense coating, having a nickel core with a calcium additive. The reduced evaporation rate from these coatings should lead to a longer service life of the cathode and of the entire device utilizing such a cathode. The increased service life of the device as a whole should occur as a result of the lesser amount of sputtering of the free barium from the cathode to other electrodes, which will, naturally, lead to the reduction in a whole series of damaging effects (emission from grids, change in the contact difference of the potentials between the electrodes, conductivity between electrodes, etc.).

4. In view of the fact that the main portion of the free barium formed as a result of the reaction between the BaO and the activator vaporizes from the coating during activation at 960°C, the role of the activating admixtures introduced into the core in significant amounts is doubtfull, especially for loose coatings.

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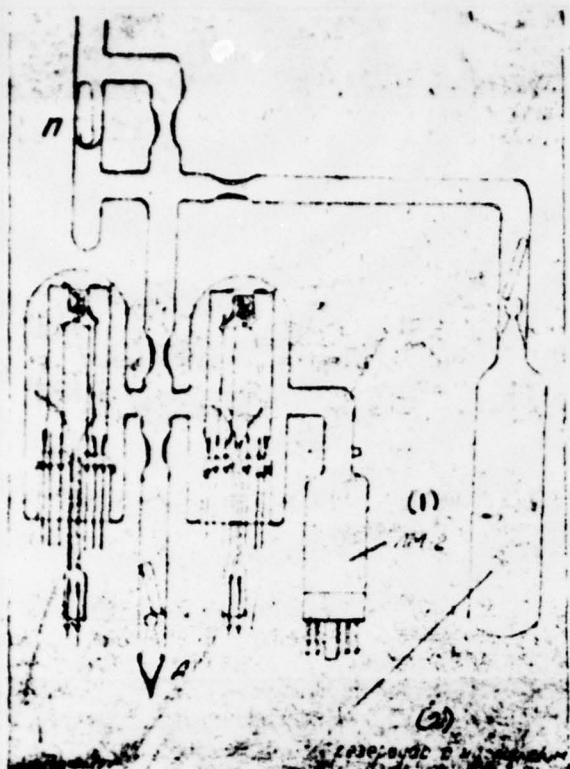
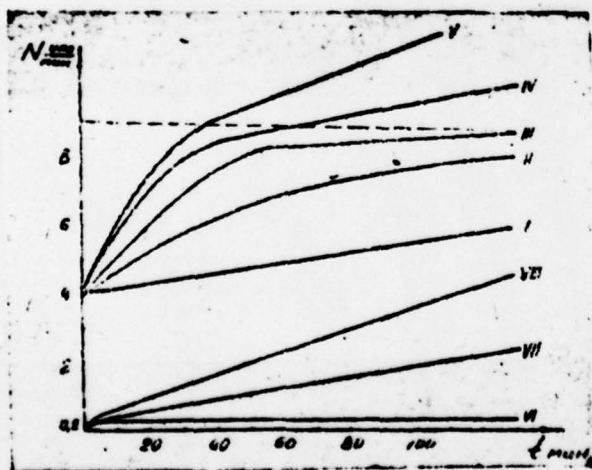Fig. 1. A device for studying the iodine vapor treatment of a cathode. Key: 1) tube 2) vessel with oxygen

Fig. 2. Curves of change in activity on cathodes No. 1 and No. 2. Cathode No. 1: VI - cathode treated below 200°C; VII - cathode treated at 350°C; and VIII - cathode treated at 370°C.

Cathode No. 2: I - cathode treated at 100°C; II - cathode treated at 150°C; III - cathode treated at 200°C; IV - cathode treated at 350°C; V - cathode treated at 370°C.

TABLE 1

(1) Тип покрытия	(2) Вес покрытия	(3) Толщина	(4) Кол-во свободного Ba в покрытии в г	(5) Кол-во свободного Ba на аноде в г
(6) Тройной мелкозернистый карбонат	(9) 1,8 мг	(10) 80 мк	$7 \cdot 10^{-7}$	$7 \cdot 10^{-6}$
(7) BaCO₃ (на воде)	(9) 1,6 мг	(10) 80 мк	$1 \cdot 10^{-5}$	$1,0 \cdot 10^{-6}$
(8) Тройной мелкозернистый карбонат (плотное покрытие)	(9) 2,2 мг	(10) 20 мк	$6 \cdot 10^{-7}$	$1 \cdot 10^{-6}$

KEY: 1) Type of coating 2) Weight of coating 3) Thickness 4) amount of free Ba in coating, in g 5) Amount of free Ba in anode, in g 6) Triple fine-grained carbonate 7) in water 8) Triple fine-grained carbonate (dense coating) 9) mg 10) μ

TABLE 2

(1) Тип покрытия	(2) Вес покрытия	(3) Толщина	(4) Кол-во свободного Ba в покрытии	(5) Кол-во свободного Ba на аноде
(6) Тройной мелкозернистый карбонат	(9) 1,8 мг	(10) 80 мк	(11) $3 \cdot 10^{-6}$ г	(11) $1,8 \cdot 10^{-5}$ г
(7) BaCO₃ (на биндере)	(9) 1,6 мг	(10) 80 мк	(11) $1 \cdot 10^{-6}$ г	(11) $3 \cdot 10^{-5}$ г
(8) Тройной мелкозернистый карбонат (плотное покрытие)	(9) 2,2 мг	(10) 20 мк	(11) $1 \cdot 10^{-6}$ г	(11) $3 \cdot 10^{-6}$ г

KEY: 1) thru 6) same as above 7) in binder 8) thru 10) same as above 11) g

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